

# Synthetic Metal Alloys: Preparation of Polyaniline/Polypyrrole Alloys in Protic Medium

Fatih KÖLELİ, Meltem DÜDÜKCÜ and Yasemin ARSLAN  
*University of Mersin, Department of Chemistry,  
Faculty of Arts and Sciences, Mersin-TURKEY*

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Pyrrole and aniline solutions were mixed in different ratios and oxidized under anodic conditions on Pt surface in protic medium. The electrocopolymerization and electrochemical properties of these alloys were investigated. Current-potential diagrams of polyaniline (PA), polypyrrole (PP) and the resulting alloys were recorded and their electrochemical characterizations were identified. In-situ resistance measurements of synthesized alloys were carried out with a home-made apparatus. Conductivity of alloys showed changes depending on applied potential as intrinsic polymers. The electrochemical behaviour of homopolymers and alloys was studied at different temperatures.

## Introduction

Developments in science and technology have revealed new application possibilities for conducting homopolymers and their derivatives<sup>1</sup>. Conducting polymers have been used widely in many areas such as rechargeable batteries<sup>2-3</sup>, condensators<sup>4</sup>, diodes<sup>5-7</sup>, LED's<sup>8</sup> and sensors<sup>9</sup>. Of this class of polymers, polyaniline and polypyrrole have been intensively studied due to their favourable processibility and relative stability<sup>10</sup>.

This wide range of application field added up to the fact that having useful conducting organic materials compared to other semiconductors and conductors increased the importance of conducting polymers<sup>11</sup>. However, their numbers are limited because of the rarity of the monomers containing conjugate  $\pi$ -electrons, which are absolutely necessary for the conductance of synthesized polymer films. The conducting organic polymers are known as synthetic metals in the literature, and the composites of different conducting polymers have been introduced by different groups<sup>12-13</sup>. Therefore in this paper, aniline-pyrrole copolymers, which we refer to as alloys to differentiate them from other widespread nonconducting copolymers, have been synthesized in different media. The aim of this work is to synthesize alloys of aniline and pyrrole in protic media, forming an alternative to intrinsic conducting polymers.

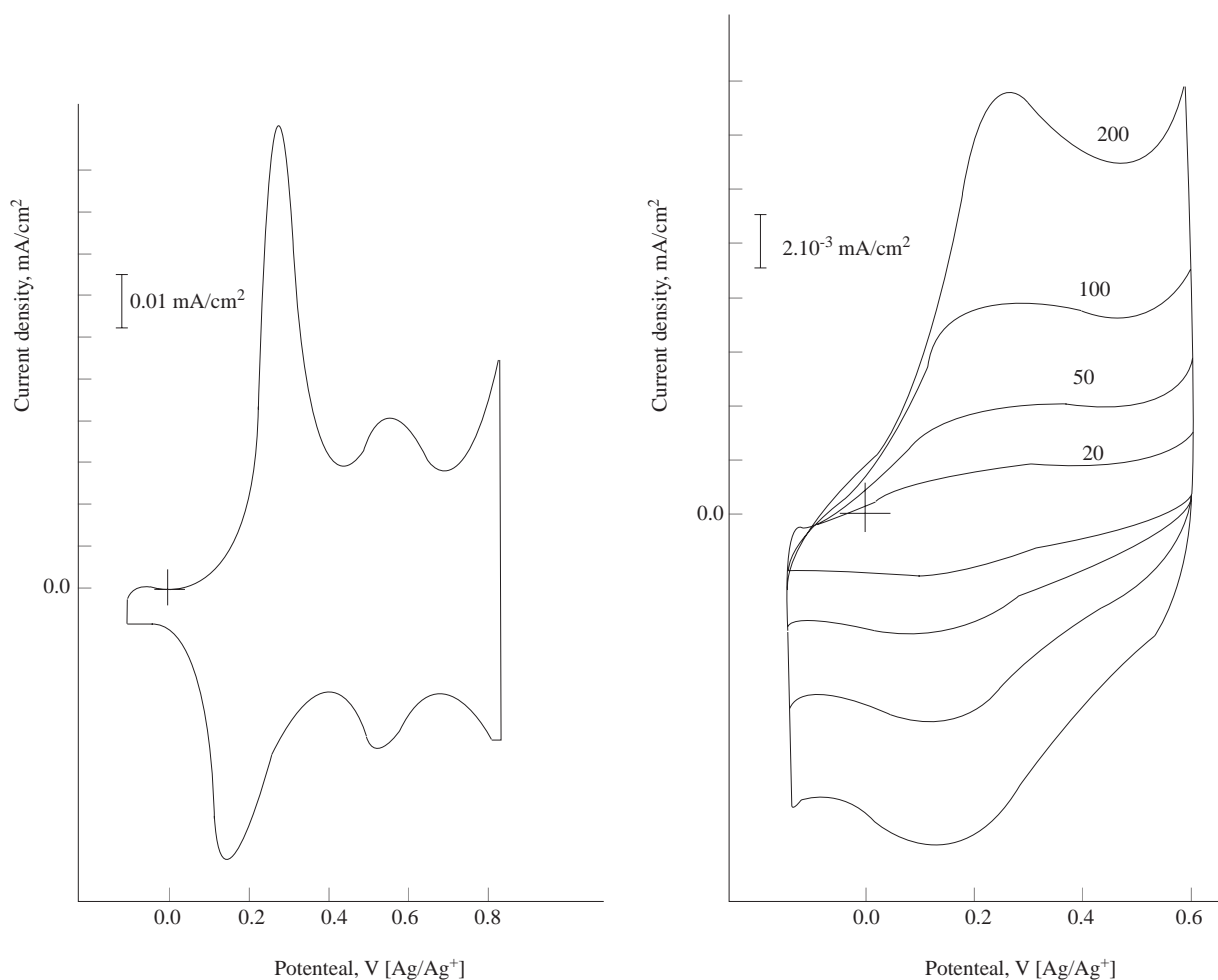
## Experimental

Aniline (Merck) and pyrrole (Fluka) were freshly distilled. Electrochemical measurements were carried out with a potentiometer, AG&G model 362, X-Y-recorder, Lloyd model PL 3. A three electrode H-cell was used for all experiments. The working and counter electrode were Pt-plates having a surface area of 1

cm<sup>2</sup>. The counter electrode was Ag/AgCl/Cl<sup>-</sup> (reference potential 1.96 vs [NHE]). The *in-situ* conductivity measurements were carried out on a home-made Wheatstone bridge, which included an oscilloscope, (Huang-Chang, model 6502), a function generator (same firm, model GFG 8017G), a resistance box (SOAR, model RD 111) and a home made capacitor box. Resistance values were recorded with a computing multimeter, TTI model 1906 (51/2 digit). The temperature measurements were carried out at 0°C, 30°C, 65°C and 80°C by a home-made thermostat. All cyclic voltammograms were recorded after the first sweep.

## Results and discussion

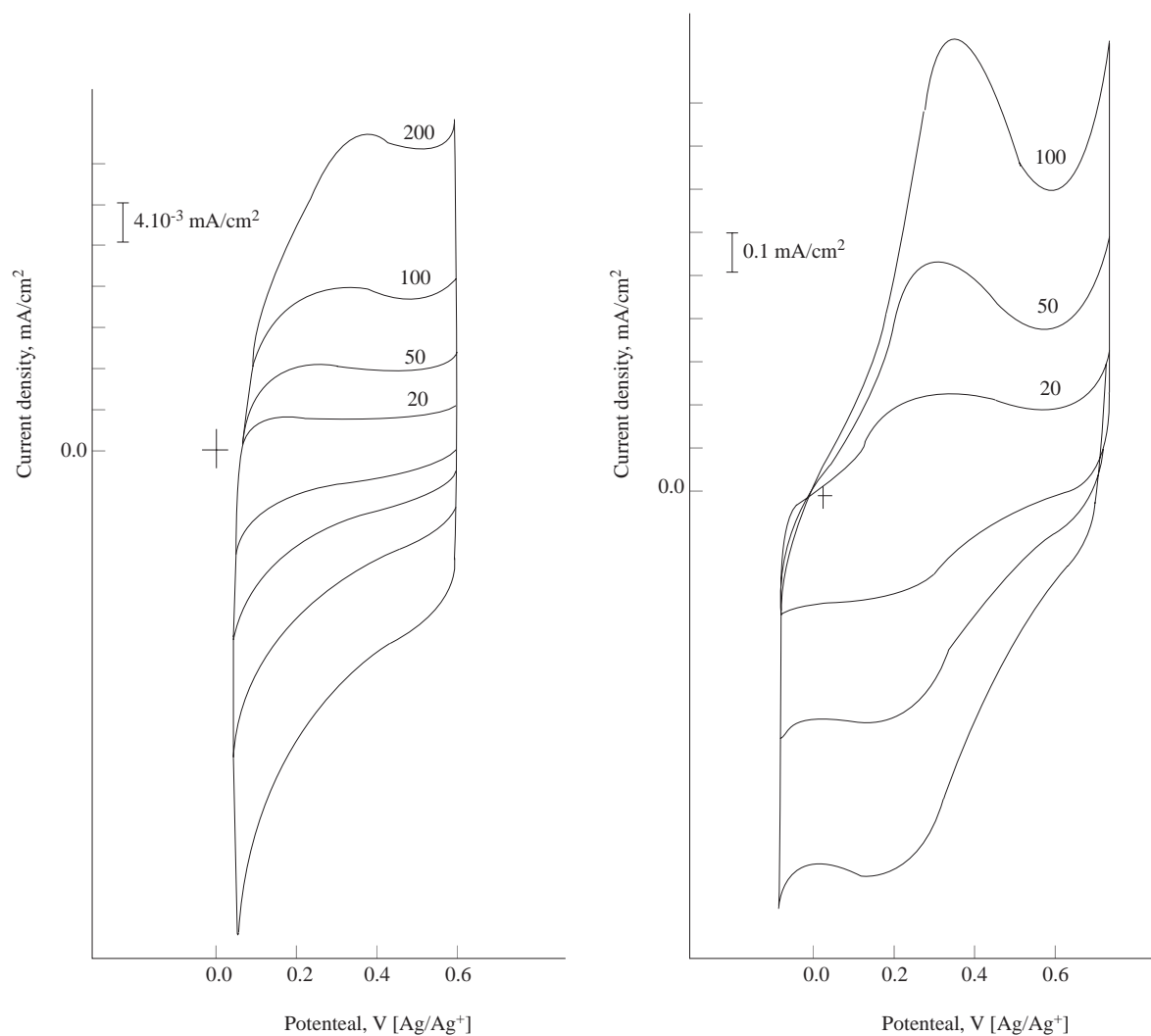
In acidic medium, the cyclic voltammograms of aniline show two oxidation waves, at 250 mV and 800 mV, which were explained as a radical cationic polaron state and a cationic bipolaron state, respectively<sup>14–15</sup>. Nevertheless, polypyrrole has only one anodic wave, in both states, polaron and bipolaron, at 250 mV in the same medium. (Figures 1a and 1b).



**Figure 1.** **a**-The cyclic voltammogram of polyaniline on Pt-electrode in 1 N H<sub>2</sub>SO<sub>4</sub> v=100 mV/s; **b**-The cyclic voltammogram of polypyrrole on Pt-electrode in 1 N H<sub>2</sub>SO<sub>4</sub>; v=20, 50,100, 200 mV/s

According to the literature<sup>16</sup>, at the first step, during the oxidation of aniline and pyrrole, radical cationic intermediates are formed. In the following steps, polymer film is produced at the potentials given

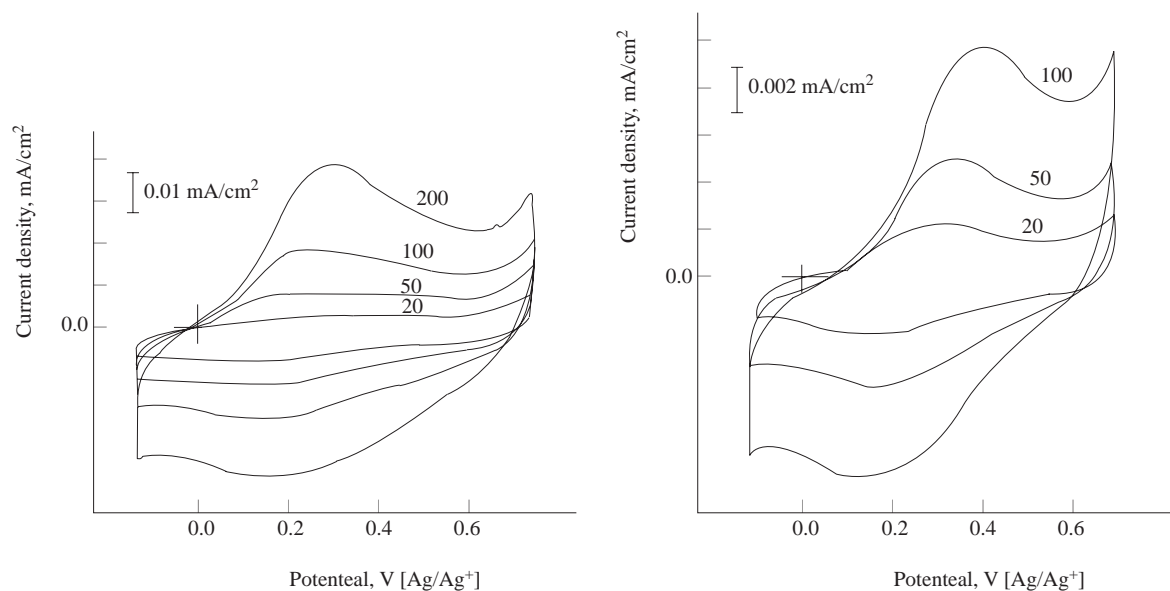
above under anodic conditions. We mixed the 0.1M solution of aniline and pyrrole in 1 N H<sub>2</sub>SO<sub>4</sub> in different proportions [1:1; 1:2; 1:3; 1:4 (v/v)] to follow the electrochemical behaviours clearly. After applying potential, we observed that some of the thin films of polymers have electrochromic properties on the electrode surface. Figures 2a and 2b show the cyclic voltammograms of the organic alloy resulting from the mixture 1:1 and 1:2 of aniline/pyrrole solution.



**Figure 2.** The cyclic voltammogram of synthesized organic alloys; **a**-1:1 mixture; **b**-1:2 mixture of 0.1 M aniline and pyrrole on Pt electrodes in 1 N H<sub>2</sub>SO<sub>4</sub>;  $v=20, 50, 100$  and  $200$  mV/s.

The voltammograms in Figures 2a and 2b have an oxidation wave at circa 300 mV and 270 mV, respectively. Pure polyaniline and polypyrrole show peaks at different potentials at approximately 250, 800 and 250 mV, respectively. Also, the form of voltammogram is different than those of polyaniline and polypyrrole. This indicates that during the oxidation of the mix solution a new electroactive material having black colour generates. The interpretation of the peak observed at ca. 50 mV was misleading and difficult. Therefore, we carried out the measurements more than three times and again we obtained the same results. Hence, we think that it belongs to H<sub>2</sub>-evolution, because the synthesized film is relatively stable in the electrolyte.

Figures 3a and 3b show cyclic voltammograms of PA/PP organic alloys with different scan rates on Pt-surface in 1 N H<sub>2</sub>SO<sub>4</sub>.



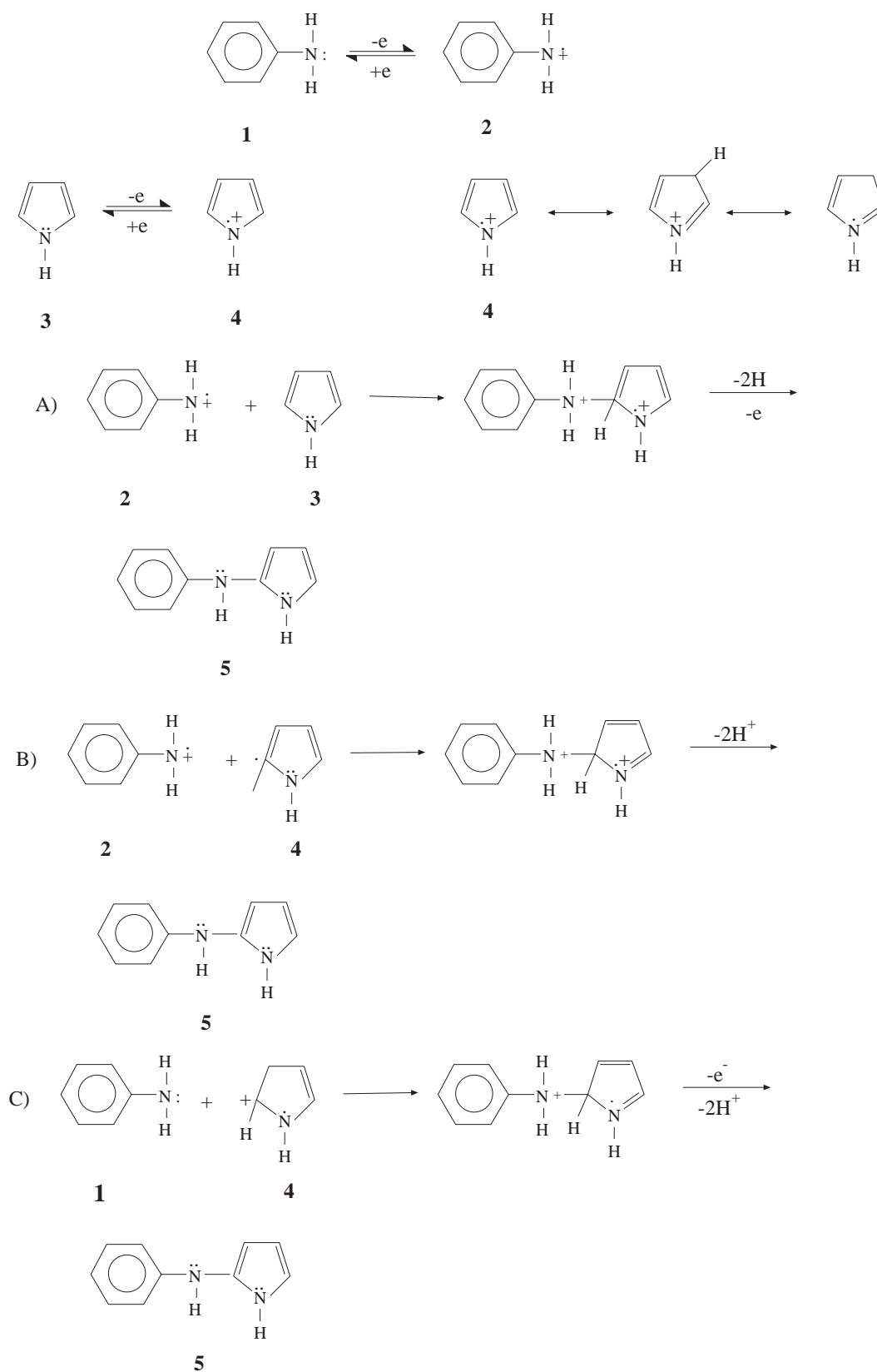
**Figure 3.** The cyclic voltammograms of synthesized organic alloys; **a**-1:3 mixture; **b**-1:4 mixture of 0.1 M aniline and pyrrole on Pt-electrodes in H<sub>2</sub>SO<sub>4</sub>.  $v = 20, 50, 100$  and  $200$  mV/s.

As seen in Figures 3a and 3b, the alloys have similar cyclic voltammetric properties to those of polypyrrole, but the peak potentials of PA/PP alloys are more positive than those of the PP-film itself, which is 250 mV. At that point, aniline molecules play an important role, so the peaks were shifted up to more positive potential values. This is expected because in the same medium the polyaniline film also shows the second peak at more positive values. All peak potentials of prepared alloys are shown in Table 1.

**Table 1.** Peak potentials of polyaniline, polypyrrole and polyaniline/polypyrrole alloys in protic medium. ( $v = 100$  mV/s.)

Polyaniline (Pa)	Pa/PP 4:1	Pa/PP 3:1	Pa/PP 2:1	Pa/PP 1:1	Pa/PP 1:2	Pa/PP 1:3	Pa/PP 1:4	Polypyrrole (PP)
1st peak 250								
2nd peak 400	360	350	340	300	270	260	240	250

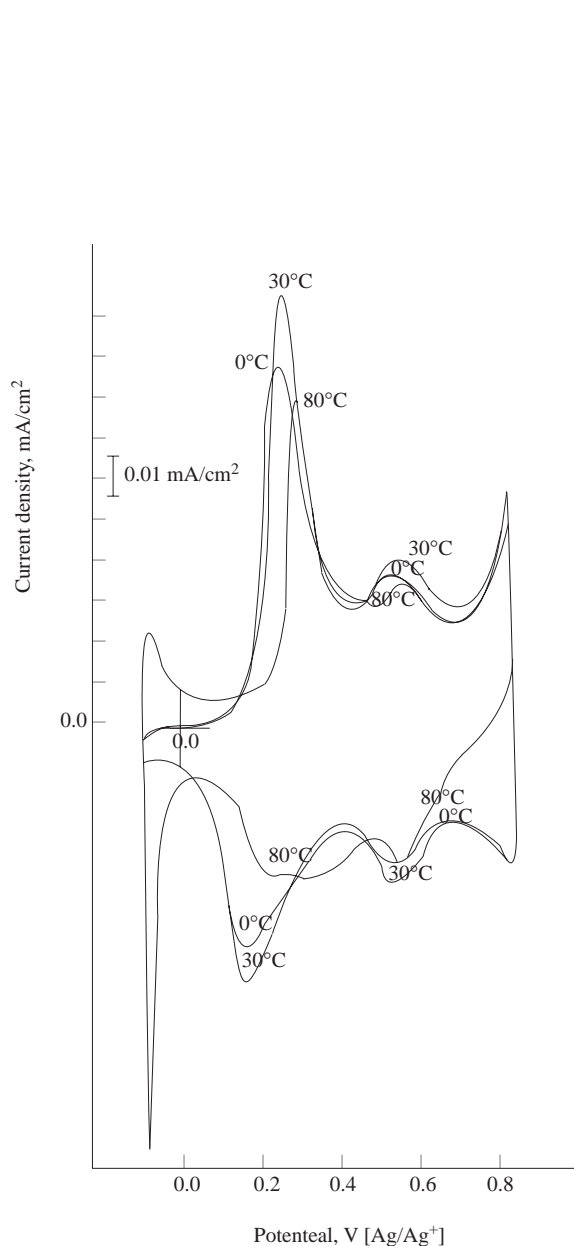
The polymerization mechanism of polyaniline and polypyrrole is described in previous works<sup>17–18</sup>. We could easily describe the reaction mechanism of the formation of the alloy, when the well known mechanisms are combined. Figure 4 shows the proposed reaction mechanism of alloy formation.



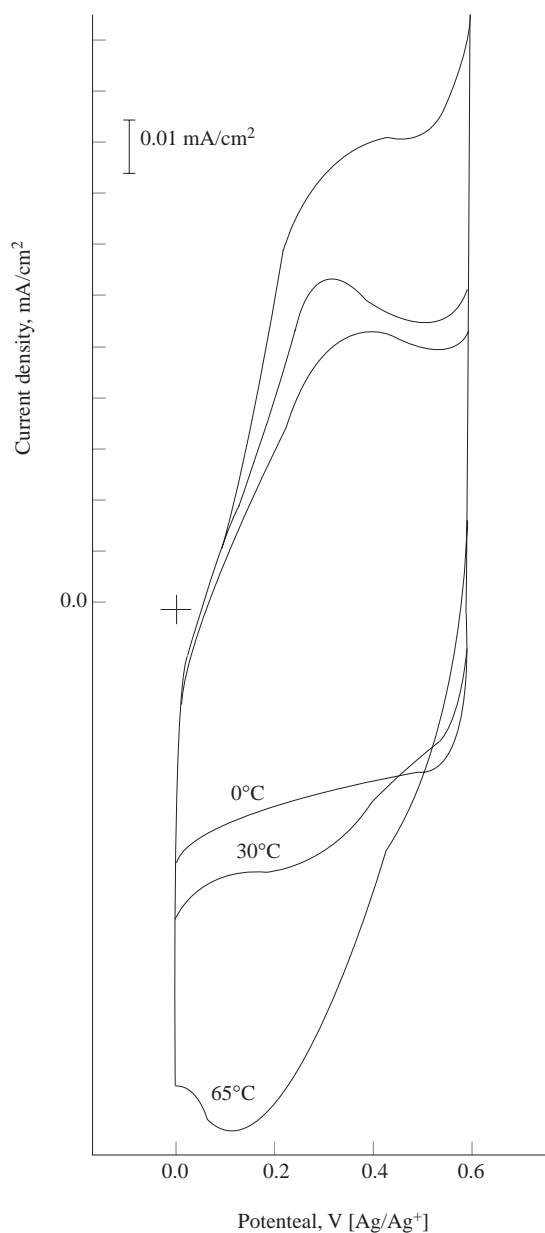
**Figure 4.** The proposed reaction mechanism of polyaniline/polypyrrole alloy formation in protic medium.

There are three possibilities to obtain compound **5**: first, an aniline radical cation can be added to the pyrrole molecule (path A); second, aniline and pyrrole radical cationic species can recombine (path B); and finally a pyrrole radical cation can be added to aniline molecule (path C). In all cases, mechanisms lead to the same product **5**, which can act as aniline and/or pyrrole for further electron transfer steps in the solution.

It is very interesting that the polyaniline film itself shows changes in CV when the temperature is raised to 80°C. The hydrogen evolution becomes remarkable and, unexpectedly, the current density decreases at higher temperatures. Also, the peak potential value is shifting to positive potentials, insignificantly (Figure 5).



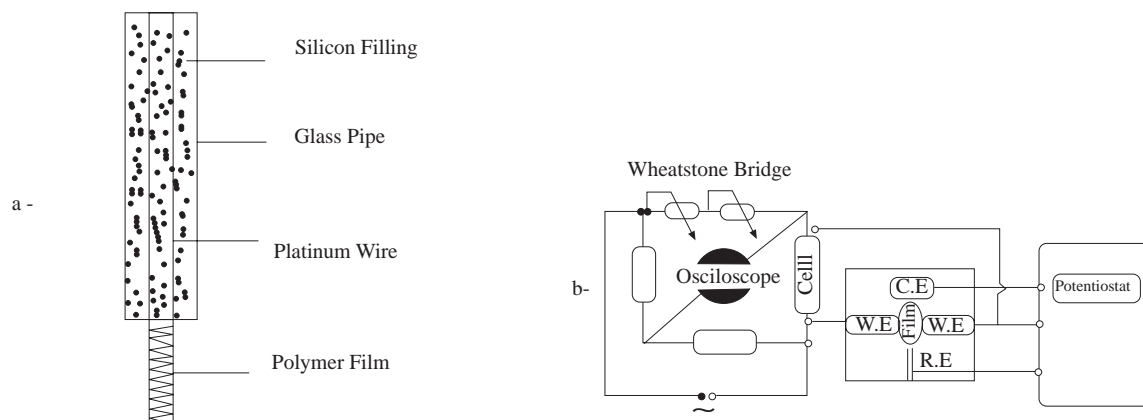
**Figure 5.** Cyclic voltammograms of polyaniline at different temperature (0, 30 and 80°C) on Pt-electrode in 1 N H<sub>2</sub>SO<sub>4</sub>;  $v=100$  mV/s



**Figure 6.** Temperature influence on the cyclic voltammogram of PA/PP 2:1 in protic medium.

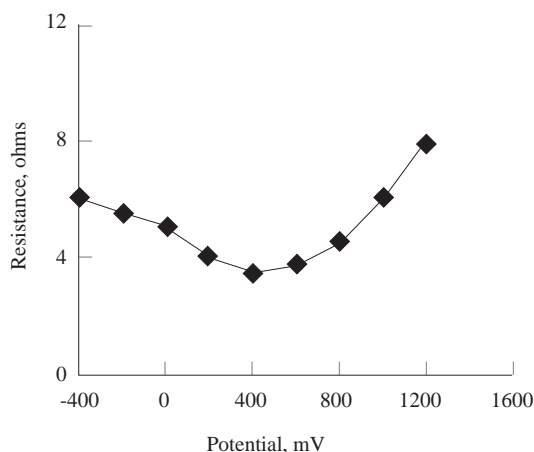
The cyclic voltammograms of synthesized alloys show deformation and shifting peak potentials increasing temperature values. The anodic peak potentials are also shifting to more negative potentials with increasing temperature. A new shoulder was observed at ca. 400 mV at 65°C in the cyclic voltammogram of PA/PP alloy (2:1) (Figure 6).

As mentioned above, the in-situ conductance measurements were carried out with the help of a Wheatstone bridge. Hence, the alloys were deposited on a special electrode consisting of two Pt wires placed in a glass tube and filled with solid silicone to keep the growing of film only on the end of the electrode. Figure 7 shows the constructed electrode and used circuit, schematically.



**Figure 7.** a- The electrode constructed for *in-situ* conductivity measurement and b- the used Wheatstone bridge circuit.

The results of the conductivity measurement show that the organic alloys behave like intrinsic homopolymers (e.g polyaniline and/or polypyrrole) and give changeable conductivity with respect to applied potential. Figure 8 shows the resistance curve of the PA/PP (2:1) alloy depending on the potential in protic medium.



**Figure 8.** The resistance-potential curve of PA/PP (2:1) alloy on Pt-electrode in 1 N H<sub>2</sub>SO<sub>4</sub>.

As shown in Figure 8, the resistance-potential curve shows a minimum at ca. 400 mV in the cyclic voltammogram. This means that the prepared organic alloy film has maximum conductivity at the mentioned potential. At more positive potentials, the resistance increases as expected.

As a result of evaluation of the cyclic voltammograms and *in-situ* conductance measurements, new conducting organic alloys suitable for different uses, such as electrode material or a semiconductor for diodes, with comparable properties were synthesized.

## Conclusion

Alloys of aniline and pyrrole were synthesized by electrochemical-oxidation by using certain amount of prepared mixtures aniline and pyrrole monomers. Current-potential diagrams of synthesized polyaniline, polypyrrole and alloys were taken and their electrochemical characterization was done. Depending on applied potential, the redox reactions occurring in polyaniline, polypyrrole and alloys of aniline and pyrrole were observed in the cyclic voltammograms. Consequently, alloys of aniline and pyrrole were observed to be electroactive like polyaniline and polypyrrole.

In-situ resistance measurements of alloys of aniline and pyrrole (1:2) were carried out in protic medium. Conductivity of alloy showed changes depending on applied potential like intrinsic polymers as well.

Electrochemical behaviour of polyaniline, polypyrrole and alloys of aniline and pyrrole were studied at different temperatures. The redox behaviour was observed in all films in the best at the ambient temperature (30°C).

## Acknowledgements

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